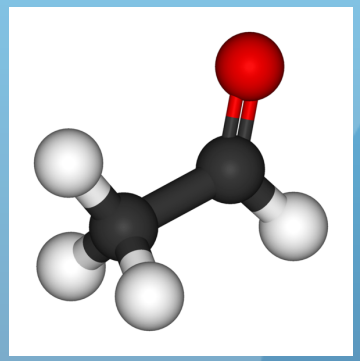
TERAHERTZ SPECTROSCOPY OF DEUTERATED ACETALDEHYDE: CH_2DCHO



L. Margulès, R. A. Motiyenko

Laboratoire PhLAM, Université de Lille1, France

L. H. Coudert

LISA, CNRS, Universités Paris Est Créteil et Paris Didero, Francet

and J.-C. Guillemin

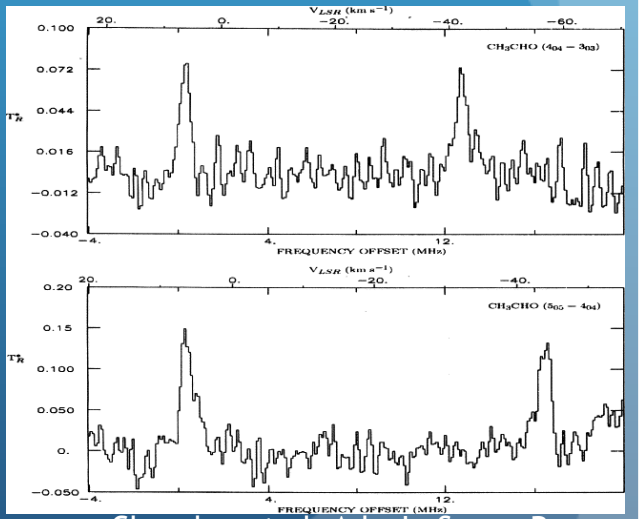
Sciences Chimiques de Rennes, ENSCR, France

Astrophysical interest: C_2H_4O isomers

- Key role in astrobiology:
  - in amino acid formation
  - early metabiotic pathways

- Its isomer (ethylene oxyde) suggests the presence of Furane (c-C_4H_4O) closely related to the sugars ribose and deoxyribose, which are central constituent of RNA and DNA

- Since its first detection in 1973 in Sgr B_2 (Gottlieb et al. « Molecules in the Galactic environment »). It has been detected in different interstellar environment:
  - Hot cores and star forming regions
  - Cold molecular clouds (10K) (Mattews et al. ApJ, 290, 609, 1985)
  - Translucent clouds (Turner et al., APJ, 518, 699, 1999)



Charnley et al. Adv. In Space Res. 33, 23, 2004

Astrophysical interest: C_2H_4O isomers

- Formation processes are still unknown:
  - the observations are giving abundances 2-600 times higher than pure gas phase models
  - Grain surface chemistry are responsible for producing these compounds
  - Bennet et al. (ApJ, 634, 698, 2005) suggest two routes to form acetaldehyde in carbon monoxide-methane and carbon dioxide-ethylene mixtures

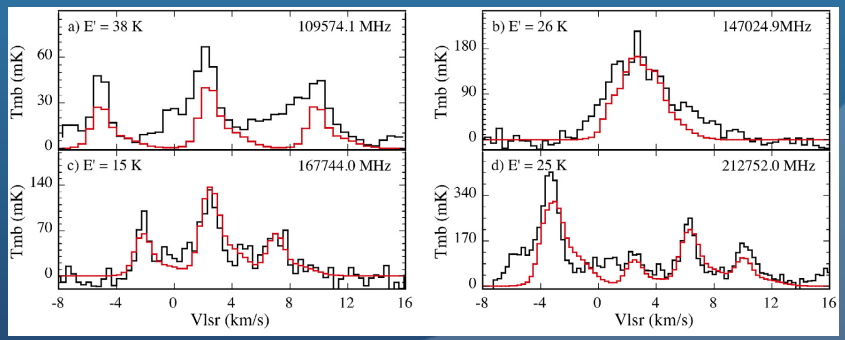
Why D-acetaldehyde?

- Among the various aspects, theits deuteration degree may provide crucial hints on its origin. In fact, highly enhanced molecular deuteration, by several orders of magnitude, has been observed in several species and sources leading to the idea that it is a memory of the past species history,namely its formation origin (Ceccarelli, C.; et al., (eds.), University of Arizona Press, Tucson, 951, (2007) 47).

- Recent studies about deuterated species of COM's permit their first detection in the ISM
  - Methyl formate in ORION: $DCOOCH_3$ (L. Margulès et al. 2010, ApJ. 714, 1120), $HCOOCH_2D$ (L. H. Coudert et al. 2013, ApJ, 779, 119)

- Dimethyl-Ether in IRAS 16293-2422: CH_2D-0-CH_3 (C. Richard et al. 2013, A&A, 552, A117)

A&A 552, A117 (2013)



Why D-acetaldehyde?

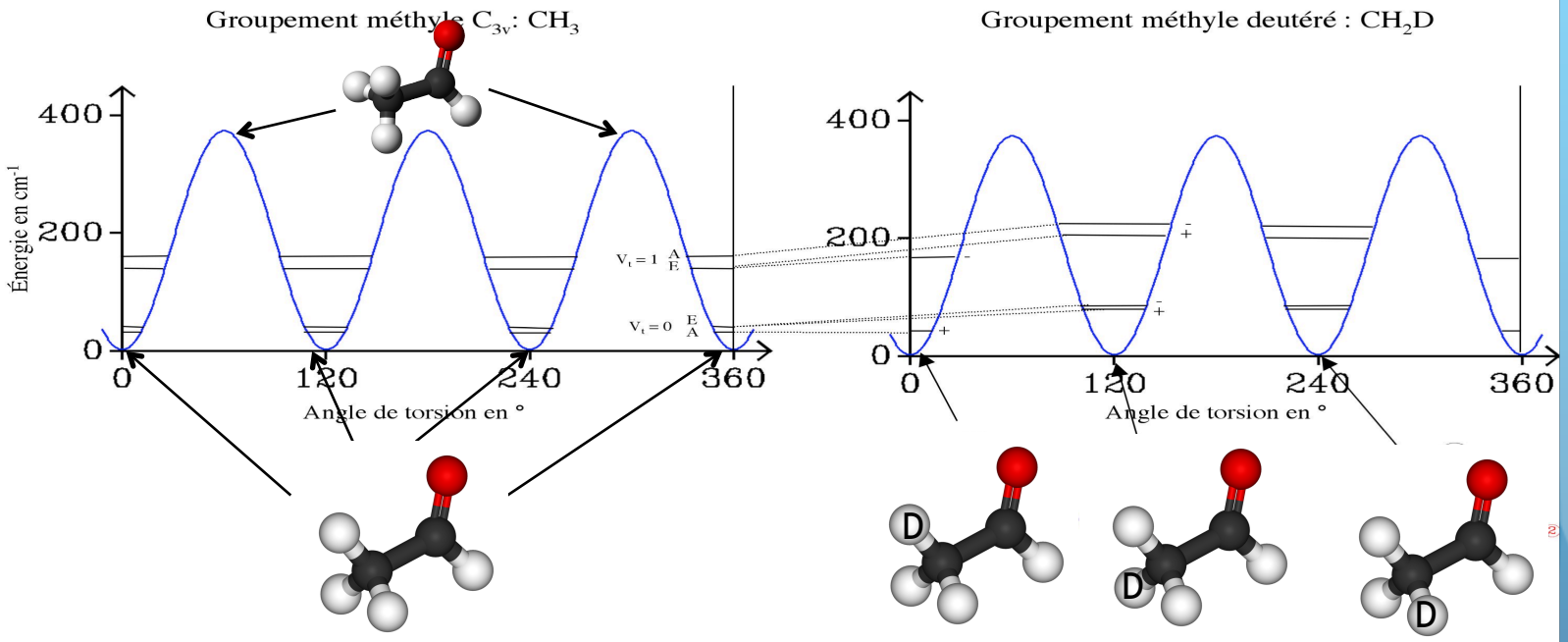
- This follows the study of the normal (I.A. Smirnov et al., 2014, JMS. 295, 44) and ^{13}C species (L. Margulès et al, Manuscript in preparation)
- Testing the limit of the water-dimer formalism used with $HCOOCH_2D$: acetaldehyde is a more complicate case than methyl-formate! (J.T. Hougen, JMS. 114 (1985) 395-426; L.H. Coudert, J.T. Hougen, JMS. 130 (1988) 86–119; L. Margulès, L.H. Coudert et al. JMS. 254 (2009) 55)

- Strong coupling between torsion and rotation: Internal rotation code necessary even for A lines: not possible to fit these lines with Watson's Hamiltonian

	V_3 in cm^{-1}	ρ
$HCOOCH_3$[a]	373	0.08
CH_3CHO[b]	408	0.33
CH_3OH[c]	374	0.81

[a]V. Ilyushin et al. J. Mol. Spectrosc. 255, 32, 2009
[b]I.A. Smirnov et al., 2014, J. Mol. Spectrosc. 295, 44
[c]L.-H. Xu et al. J. Mol. Spectrosc. 251, 305, 2008

Internal rotation motion



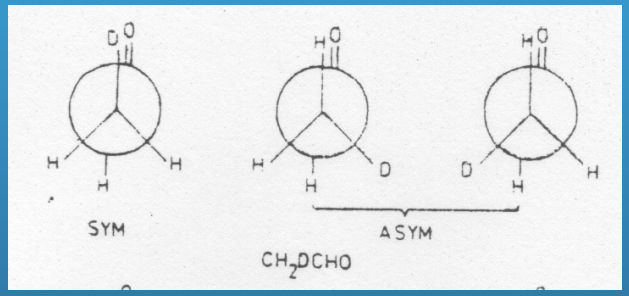
Due to tunnel effect, the transitions are splitted into two components: A et E

Each transition is splitted into 3 components :

- configuration D in the plane
- tunnel effect between the 2 equivalent configurations D-out of plan

Previous studies about D-CH_3CHO

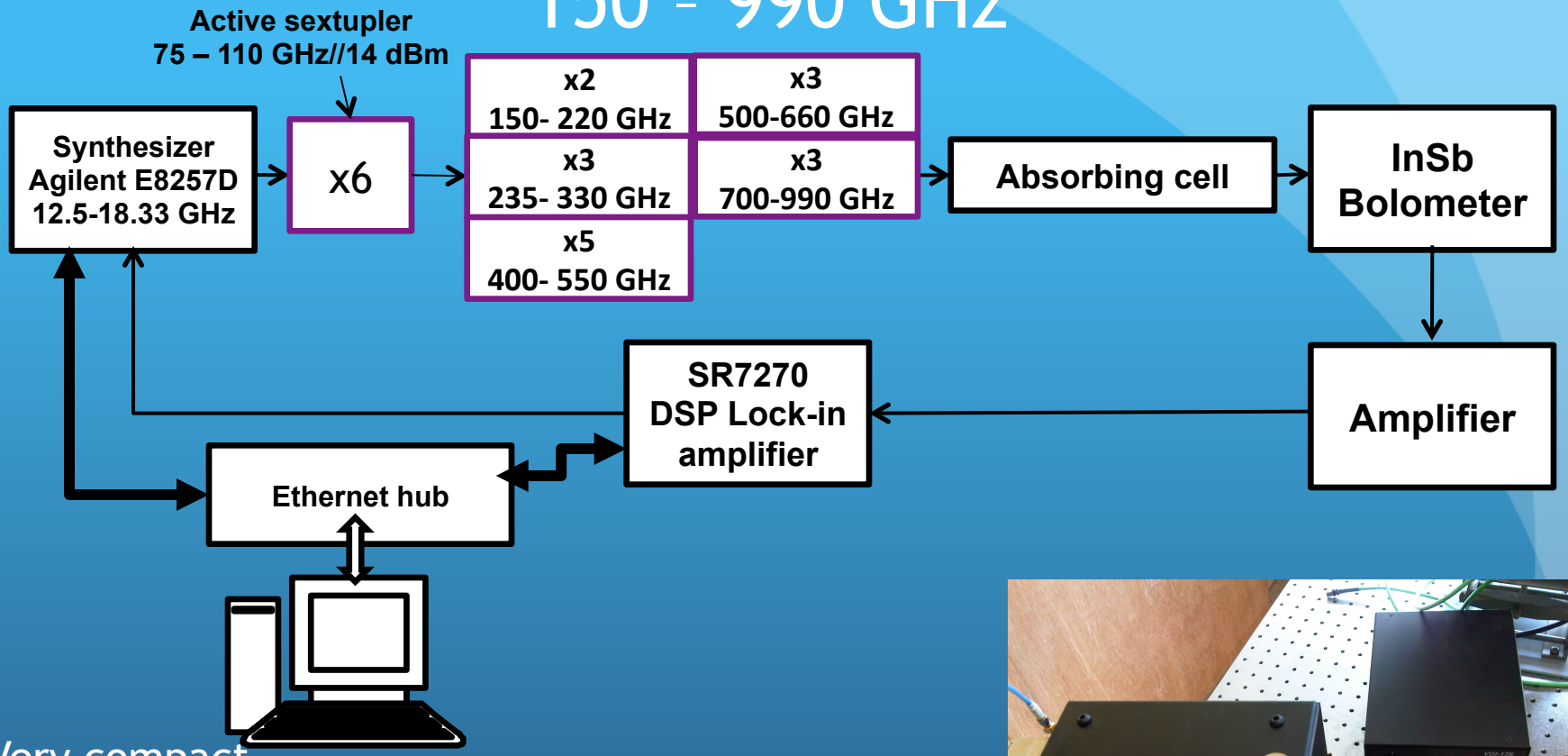
- CD_3CHO up to 250 GHz (Kleiner et al. J. Mol. Spectrosc. 197, 275, 1999)
- CH_3CDO up to 380 GHz (Elkeurti et al. J. Mol. Spectrosc. 263, 145, 2010)
- CD_3CDO up to 40 GHz (Kilb et al. J. Chem. Phys. 26, 1695, 1957)
- CH_2DCHO up to 40 GHz (no commercial sample)

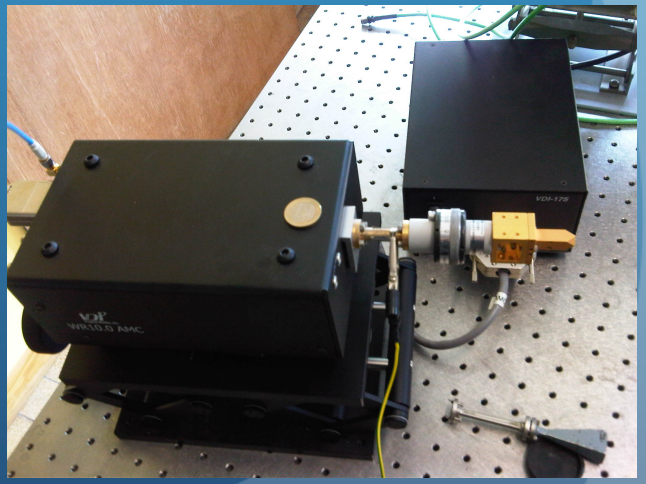


- Sym-species (Turner, P. H.et al.Chem. Phys. Lett. 42, (1976) 84)
- Asym-species (Turner, P. H. et al. J.C.S. Farady Trans. 2 77, (1981) 1217)
- Dipole moment (Turner, P. H. et al. J.C.S. Farady Trans. 2, 74, (1978) 533)

μ_a= 2.46 D and μ_b = 1.156 D

Solid state sources spectrometer: 150 – 990 GHz





- Very compact
- power : 50 mw – 5mW)
- Broad band : Assigment easier with series, like in I. R.
- Full coverage with high resolution in 5 days

Spectra

- The spectra is dense even if the molecule is relatively light (44g.mol^{-1})
  - μ_a and μ_b spectra, instense up to submillimeterwave range (respectively 2.46D amd 1.156 D)
  - Each lines is split in 3 components
  - 1st torsional state is lying at 143 cm^{-1} (^{12}C value), relative intensity to g.s. is 50%
- If it is not enough…

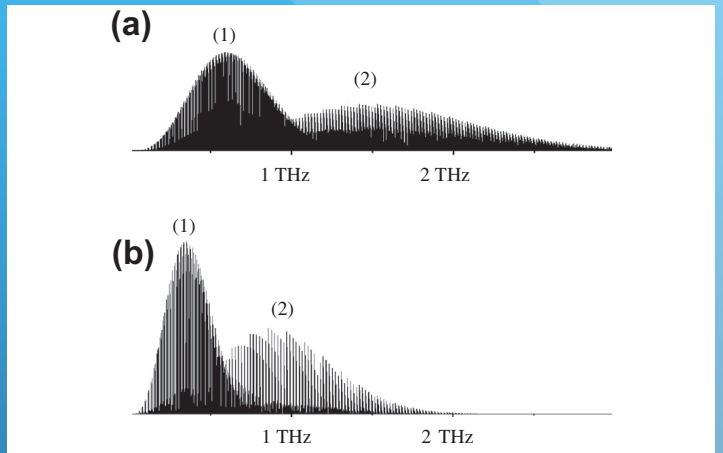
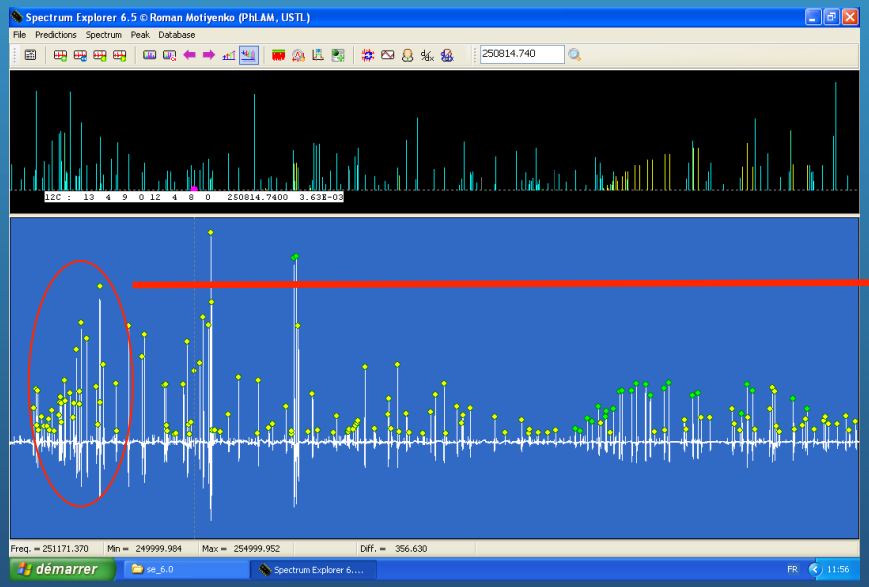


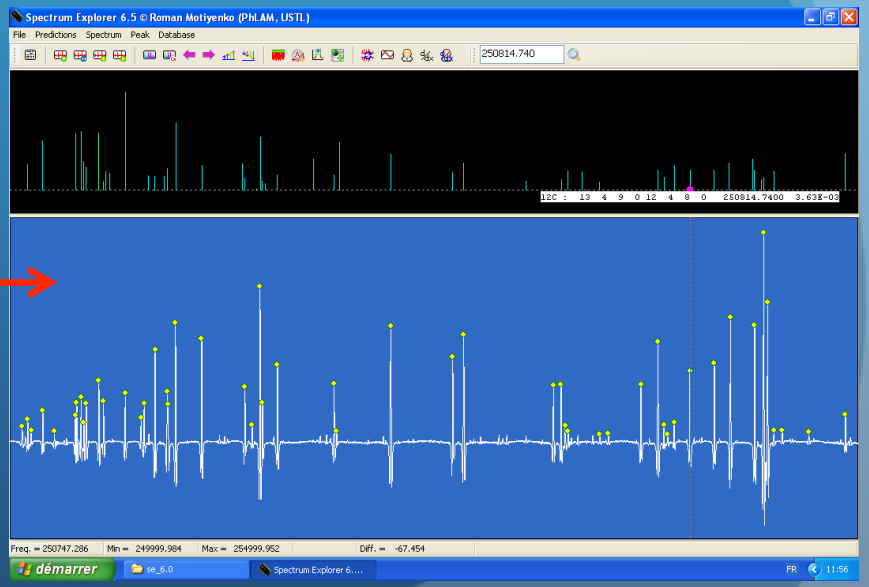
Fig. 2. Predicted rotational spectrum for the $v_t = 0,1,2$ torsional states of acetaldehyde at 300 K (a) and 100 K (b). In both cases maximum (1) in intensity distribution corresponds to $^{a}R_{0,1}$-type transitions with low K_a values, whereas maximum (2) corresponds to $^{b}R_{1,\pm1}$ type transitions with the K_a numbers approaching the J values.

I.A. Smirnov et al., 2014, JMS. 295, 44)

The sample

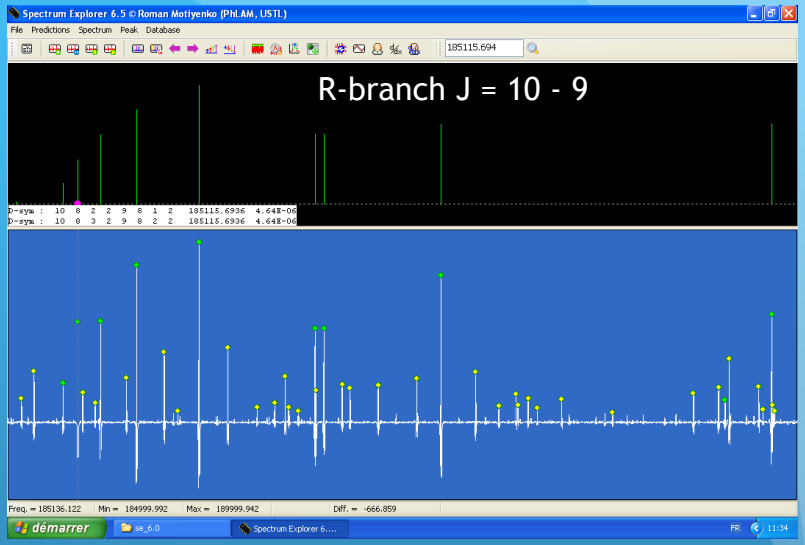
- Depending of the fill-in, we have 1/ 3 to 1/2 of normal species.
- Prediction are accurate up to 1.6 THz but this increase density of the spectra and complicate the analysis

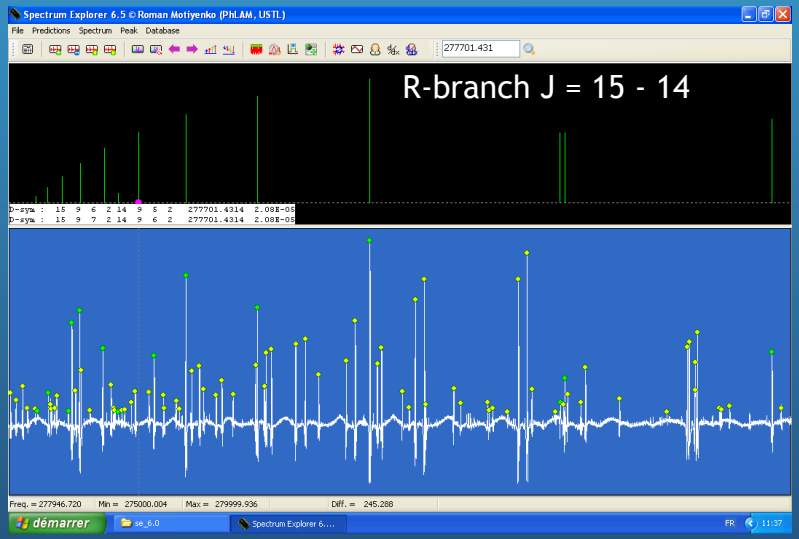


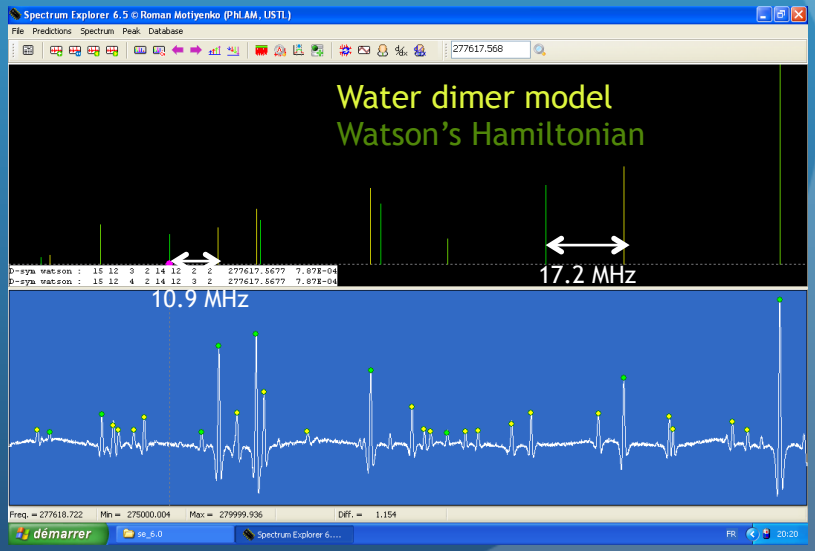


Perturbation between conformers

- With Methyl-formate ($HCOOCH_2D$), the in-plane conformer could be treated with Watson-type Hamiltonian: no perturbation appeared
- Up to J=12, no problem…

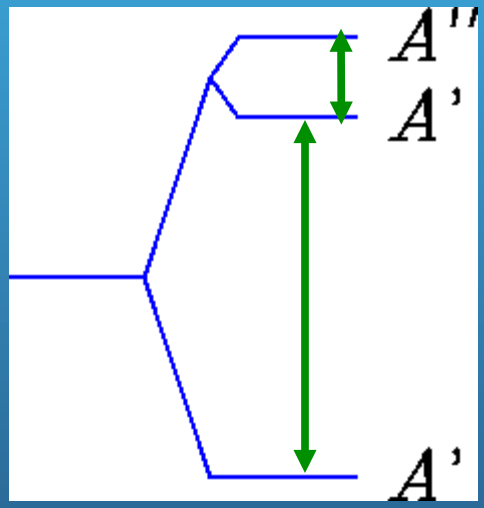






Energy between conformers

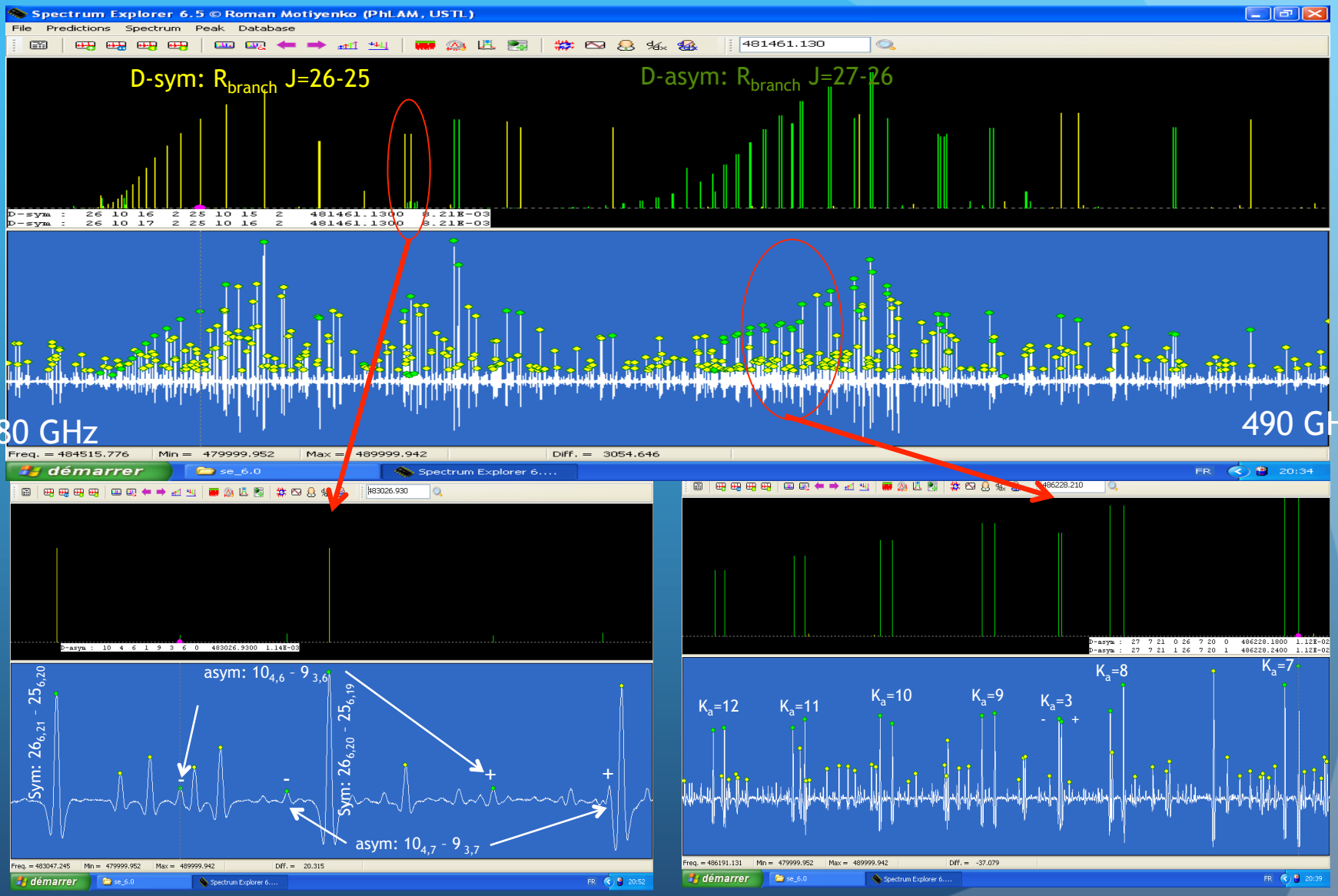
- These perturbations permits to determine the energy difference between the 2 conformers



$HCOOCH_2D$	CH_2DCHO
84.8 MHz	804.059 MHz
10 cm^{-1}[a]	15.56 cm^{-1}

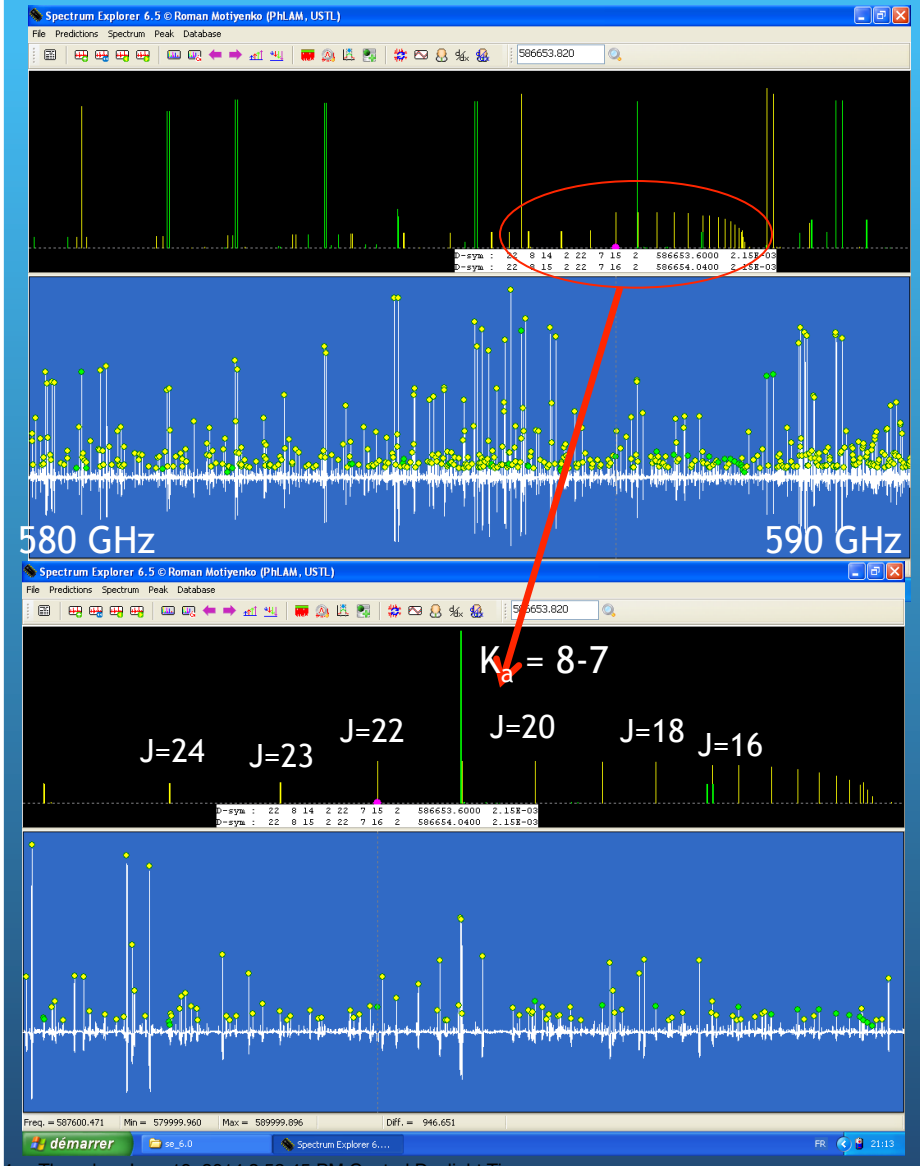
[a]Estimated from C. R. Quade and Chun C. Lin, J. Chem. Phys. 38 (1963) 540

Assignment

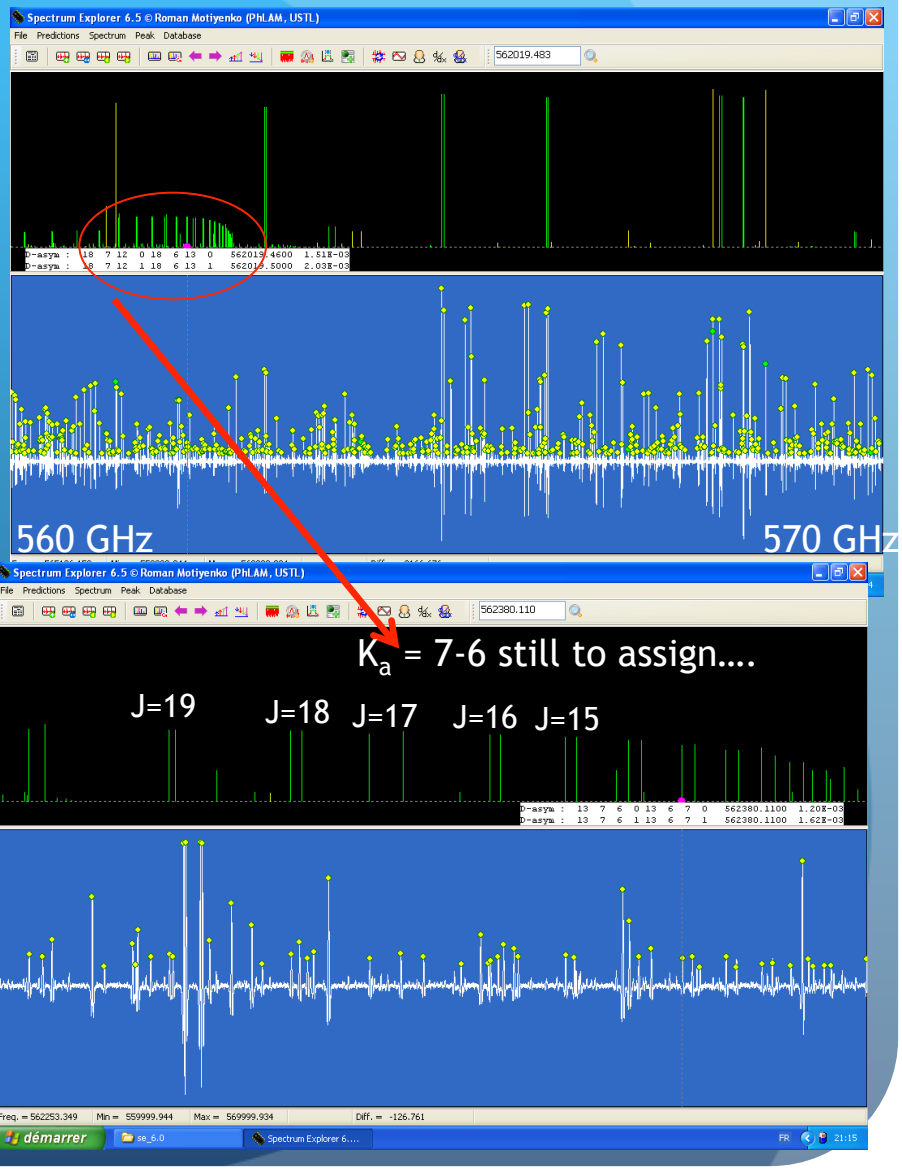

Spectrum Explorer 6.5 © Roman Motiyenko (PhLAM, USTL)
File Predictions Spectrum Peak Database
D-sym: R branch J=26-25
D-asym: R branch J=27-26
480 GHz
490 GHz
asym: 10 4,6 - 9 3,6
Sym: 26 6,21 - 25 6,20
Sym: 26 6,20 - 25 6,19
asym: 10 4,7 - 9 3,7
Ka=12
Ka=11
Ka=10
Ka=9
Ka=3
Ka=8
Ka=7

Assignment Q branch

D –in plane



D –out of plane



Results

	In-plane		Out-of plane	
	Turner et al.	This work	This work	Turner et al.
Rot.+Dist. terms	8	12	12	8
Tunelling terms			14	4
In-out of plane coupling terms		9		
$\Delta E_{\text{in-out}}(cm^{-1})$		15.558550(78)		15.55(fixed)
$\Delta E_{\text{tunelling}}$ (MHz)			804.059(33)	804.5
$N_{\mu a}$ J_{max}; $K_{a,max}$	22 – 20 - 3	460 – 34 - 20	482 – 28 - 9	38 – 20 - 3
$N_{\mu b}$ J_{max}; $K_{a,max}$	39 – 20 - 6	442 – 35 - 8	122 – 29 - 4	30 – 18 - 3
$N_{\mu c}$ J_{max}; $K_{a,max}$			17 – 10 - 4	24 – 18 - 3
F_{max} in GHz	40	600	500	40
rms	480 kHz	48 kHz	83 kHz	231 kHz

Conclusions - Perspective

- Water dimer formalism could be used with more complex case than methyl formate
- The energy difference between the in and out-of plane conformers could be determined
- The spectra should be assign up to 990 GHz
- The D-methanol approach will be test at the end to compare the quality of the fit (less parameters needed?)
- This work could be useful to detect it in high deutarated objects like hot corino

Aknowledgements

- Action sur Projets de l'INSU : "Physique et Chimie du Milieu Interstellaire"
- Centre National d'Etudes Spatiales (CNES)

And many thanks for your attention